Article

Exhaust Emissions of Biodiesel, Petrodiesel, Neat Methyl Esters, and Alkanes in a New Technology Engine

Gerhard Knothe, Christopher A. Sharp, and Thomas W. Ryan

Energy Fuels, **2006**, 20 (1), 403-408 • DOI: 10.1021/ef0502711

Exhaust Emissions of Biodiesel, Petrodiesel, Neat Methyl Esters, and Alkanes in a New Technology Engine†

Gerhard Knothe,*,‡ Christopher A. Sharp,§ and Thomas W. Ryan, III§

National Center for Agricultural Utilization Research, Agricultural Research Service, U.S. Department of Agriculture, Peoria, Illinois 61604, and Engine and Vehicle Research Division, Southwest Research Institute, San Antonio, Texas 78288

Received August 22, 2005. Revised Manuscript Received November 15, 2005

Biodiesel is a renewable, alternative diesel fuel of domestic origin derived from a variety of fats and oils by a transesterification reaction; thus, it consists of the alkyl esters, usually methyl esters, of the fatty acids of the parent oil or fat. An advantage of biodiesel is its potential to significantly reduce most regulated exhaust emissions, including particulate matter (PM), with the exception of nitrogen oxides (NO_x). In this work, three fatty acid methyl esters, neat methyl laurate, neat methyl palmitate, and technical grade methyl oleate, were selected for exhaust emissions testing in a heavy-duty 2003 six-cylinder 14 L diesel engine with exhaust gas recirculation. These fuels were compared with neat dodecane and hexadecane as well as commercial samples of biodiesel and low-sulfur petrodiesel as the base fuel, thus establishing for the first time a baseline of the exhaust emissions of neat hydrocarbon (alkane) fuels versus neat methyl esters. All fuels were tested over the heavy-duty diesel transient cycle. PM emissions were significantly reduced with biodiesel and methyl oleate (about 77 and 73%, respectively), while reductions with methyl palmitate and methyl laurate were even greater (82−83%) compared to the petrodiesel fuel. PM emissions with biodiesel only slightly exceeded the upcoming emissions standards, raising the possibility that biodiesel may meet these standards using only a diesel oxidation catalyst without employing a particulate trap. NO_x emissions increased with biodiesel (about 12%) and technical grade methyl oleate (about 6%) but decreased (about 4−5%) with methyl palmitate and methyl laurate relative to those of the base fuel. PM emissions decreased (about 45−50%) with both dodecane and hexadecane. NO_x emissions were reduced (around 15.5−16%) with dodecane and hexadecane compared to those of the petrodiesel fuel. The methyl ester moiety influences exhaust emissions by reducing particulate matter considerably more than neat straight-chain hydrocarbons, which are enriched in “clean” petrodiesel fuels, while NO_x exhaust emissions, which showed little chain-length dependence, are less reduced. Thus, no future “clean” petrodiesel fuel should be able to achieve the low PM exhaust emissions levels of biodiesel without additional additive treatments or support by engine technology. Unsaturated fatty esters show slightly increased NO_x and PM emissions compared to their saturated counterparts. The soluble organic fraction of the PM emissions was higher for the ester fuels. Hydrocarbon (HC) and CO exhaust emissions were also determined. Although HC emissions were low, a strong effect of chain length was observed.

Introduction

Biodiesel[1,2] is defined as the mono-alkyl esters of vegetable oils or animal fats. It can also be derived from used frying oils. Biodiesel is produced by transesterifying the parent oil or fat to achieve a viscosity close to that of petrodiesel. Biodiesel standards have been developed in the United States, Europe, and elsewhere around the world. Advantages of biodiesel include domestic origin, reducing the dependency on imported petroleum, biodegradability, high flash point, and inherent lubricity in the neat form.[1,2] Improvement of the oxidative stability and low-temperature properties remain technical challenges. Most regulated exhaust emissions (particulate matter = PM, hydrocarbons = HC, carbon monoxide = CO) with the exception of nitrogen oxides (NO_x) are reduced through the use of biodiesel.[3−5] Thus, the reduction of NO_x exhaust emissions is another technical challenge facing biodiesel, especially in light of the increasingly stringent exhaust emissions regulations affecting diesel engines and becoming effective in the next few years (Table 1). This development is connected with the introduction of ultralow sulfur diesel fuel (ULSD; for example, less than 15 ppm sulfur in the United States). Several engine or aftertreatment technologies, such as selective catalytic reduction (SCR), exhaust gas recirculation (EGR), diesel oxidation catalysts

* To whom correspondence should be addressed. Phone: +1-309-681-6112. Fax: +1-309-681-6340. E-mail: knothegh@ncaur.usda.gov.

† Disclaimer: Product names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

‡ U.S. Department of Agriculture.

§ Southwest Research Institute.

(1) Knothe, G., Krahl, J., Van Gerpen, J., Eds. *The Biodiesel Handbook*; AOCS Press: Champaign, IL, 2005.

(2) Mittelbach, M.; Remschmidt, C. *Biodiesel*−*The Comprehensive Handbook*; Karl-Franzens University: Graz, Austria, 2004.

(3) McCormick, R. L.; Alleman, T. L. Effect of Biodiesel Fuel on Pollutant Emissions from Diesel Engines. In *The Biodiesel Handbook*; Knothe, G., Van Gerpen, J., Krahl, J., Eds.; AOCS Press: Champaign, IL, 2005; pp 165−174.

(4) Krahl, J.; Munack, A.; Schröder, O.; Stein, H.; Bünger, J. Influence of Biodiesel and Different Petrodiesel Fuels on Exhaust Emissions and Health Effects. In *The Biodiesel Handbook*; Knothe, G., Van Gerpen, J., Krahl, J., Eds.; AOCS Press: Champaign, IL, 2005; pp 175−182.

(5) *A Comprehensive Analysis of Biodiesel Impacts on Exhaust Emissions*; U.S. EPA Draft Technical Report 420-P-02-001; National Service Center for Environmental Publications: Cincinnati, OH, October 2002; http://www.epa.gov/otaq/models/analysis/biodsl/p02001.pdf.

10.1021/ef0502711 CCC: $33.50
Published on Web 11/30/2005

Table 1. Regulated Exhaust Emissions[a]

regulation	exhaust emissions species HC	CO	NO_x	PM
United States 2007 (15 ppm sulfur petrodiesel)	0.14 g/hp h NMHC	15.5 g/hp h	0.20 g/hp h	0.01 g/hp h
Euro IV 2005[b]	0.46 g/kWh	1.5 g/kWh	3.5 g/kWh	0.02 g/kWh
Euro V[b]	0.46 g/kWh	1.5 g/kWh	2.0 g/kWh	0.02 g/kWh

[a] On-highway heavy-duty diesel engines; maximum 15 ppm sulfur in the United States, 10 ppm sulfur in Europe; 1 g/hp-hr = 1.341 g/kWh. [b] Euro IV and V include smoke limited to 0.5 m^{-1}.

(DOC), as well as NO_x or particulate traps, with the goal of reducing exhaust emissions to the future low levels are being applied or are under evaluation[6−7] and will affect how any diesel fuel, including biodiesel, will meet these standards.

The impacts on exhaust emissions from the use of B20 (20 vol % biodiesel blended with petrodiesel) for soybean-based biodiesel added to an average base fuel were an increase in NO_x by 2.0% and reductions in PM by 10.1%, hydrocarbons by 21.1%, and CO by 11.0%. For neat biodiesel, the numbers show an increase in NO_x by 10% and reductions in PM by 48%, HC by 77%, and CO by 48%.[3,5] However, engine technology can significantly affect the level of exhaust emissions.[5−8] For example, it was stated that the cetane number has less effect on NO_x in EGR engines than in engines without EGR.[5] Previously, a connection between increased fuel cetane number and reduced NO_x exhaust emissions was reported.[9] The bulk modulus of fuels, which affects the spray characteristics upon injection,[10] is higher for biodiesel than for petrodiesel,[11−13] with a resulting effect on injection timing; this has been proposed to be a physical property responsible for the increase in NO_x exhaust emissions observed with biodiesel, as has kinematic viscosity.[14] Various approaches for reducing NO_x exhaust emissions when using biodiesel, including the use of additives, blending with other diesel fuels, and modifying feedstock composition, especially reducing unsaturation, have been proposed.[15−17] In addition to regulated exhaust emissions, biodiesel also has a positive effect on the levels of unregulated emissions such as nitropolyaromatic hydrocarbons.[18]

In exhaust emissions studies, biodiesel, usually commercial biodiesel, consisting of a variety of esters of fatty acids corresponding to the fatty acid profile of the parent oil or fat and containing small amounts of contaminants resulting from its production, was compared to petrodiesel of varying specifications. A previous study[19] showed that the structure of fatty compounds can have a significant effect on exhaust emissions. Results from this investigation[19] using a 1991 six-cylinder 345 hp (257 kW) direct-injected turbocharged intercooled engine on technical grade (i.e., enriched) fatty esters showed that double bonds and decreasing chain length increase NO_x exhaust emissions, while particulate matter (PM) emissions were essentially identical if the fuel density was below 0.89 g/cm^3 or the cetane number was approximately 45 or greater. Methyl and ethyl esters of the same fatty acids did not cause significant exhaust emissions differences.[19] Other previous studies compared various petrodiesel diesel fuels to biodiesel fuels with differing results for the emissions levels depending on the fuels compared.[20−21]

Information on the interaction of biodiesel with heavy-duty newer-technology engines, including the effect of the compound structure of neat or enriched components of biodiesel on exhaust emissions in comparison to neat hydrocarbon components of petrodiesel under these conditions, has been lacking. For this reason, the exhaust emissions generated by two neat saturated fatty acid methyl esters and technical grade methyl oleate in comparison to a low-sulfur commercial petrodiesel fuel, a commercial biodiesel fuel, and neat hexadecane and dodecane in a more recent (2003 model year) heavy-duty diesel engine were studied here. Hexadecane and dodecane are straight-chain alkanes, which constitute an “ideal” petrodiesel fuel, and thus, they offer the opportunity of comparing possible “ultra-clean” (low or no sulfur) petrodiesel fuels to biodiesel and its components. Also, since the petrodiesel fuels used for comparison with biodiesel or its components in other studies vary in composition, using these neat alkanes establishes a baseline of hydrocarbons (alkanes) versus methyl esters for the first time. All regulated exhaust emissions species (CO, hydrocarbons, NO_x, and PM) were determined. Particulate matter was analyzed for the amount of the soluble organic fraction (SOF).

Experimental Section

Although all emissions values are given here in grams per horsepower hour (g/hp hr, corresponds to g/bhp hr), it is important to note that they can be easily converted to grams per kilowatt hour (g/kWh) using the relation 1 g/hp hr = 1.341 g/kWh.

The petrodiesel fuel (EPA Certification grade; 350 ppm sulfur) was obtained from Chevron-Phillips, and the commercial soy-based biodiesel fuel was produced by West Central Soy (Ralston, IA). GC-MS analysis of the petrodiesel fuel is depicted in Figure 1.

(6) McGeehan, J. A. Diesel Engines Have a Future and That Future is Clean. *SAE Tech. Pap. Ser.* **2004**, 2004-01-1956.

(7) *Diesel Exhaust Emission Control 2005*; SAE Special Publication SP-1942; Society of Automotive Engineers: Warrendale, PA, 2005.

(8) Sharp, C. A.; Howell, S. A.; Jobe, J. The Effect of Biodiesel Fuels on Transient Emissions from Modern Diesel Engines, Part I Regulated Emissions and Performance. *SAE Tech. Pap. Ser.* **2000**, 2000-01-1967.

(9) Ladommatos, N.; Parsi, M.; Knowles, A. The Effect of Fuel Cetane Improver on Diesel Pollutant Emissions. *Fuel* **1996**, *75*, 8−14.

(10) Varde, K. S. Bulk Modulus of Vegetable Oil−Diesel Fuel Blends. *Fuel* **1984**, *63*, 713−715.

(11) Tat, M. E.; Van Gerpen, J. H.; Soylu, S.; Canakci, M.; Monyem, A.; Wormley, S. The Speed of Sound and Isentropic Bulk Modulus of Biodiesel at 21 °C from Atmospheric Pressure to 35 MPa. *J. Am. Oil Chem. Soc.* **2000**, *77*, 285−289.

(12) Tat, M. E.; Van Gerpen, J. H. Speed of Sound and Isentropic Bulk Modulus of Alkyl Monoesters at Elevated Temperatures and Pressures. *J. Am. Oil Chem. Soc.* **2003**, *80*, 1249−1256.

(13) Boehman, A. L.; Morris, D.; Szybist, J. The Impact of the Bulk Modulus of Diesel Fuels on Fuel Injection Timing. *Energy Fuels* **2005**, *18*, 1877−1882.

(14) Choi, C. Y.; Reitz, R. D. A Numerical Analysis of the Emissions Characteristics of Biodiesel Blended Fuels. *J. Eng. Gas Turbines Power* **1999**, *121*, 31−37.

(15) McCormick, R. L.; Alvarez, J. R.; Graboski, M. S.; Tyson, K. S.; Vertin, K. Fuel Additive and Blending Approaches to Reducing NO_x Emissions from Biodiesel. *SAE Tech. Pap. Ser.* **2002**, 2002-01-1658.

(16) Szybist, J.; Simmons, J.; Druckenmiller, M.; Al-Qurashi, K.; Boehman, A.; Scaroni, A. Potential Methods for NO_x Reduction from Biodiesel. *SAE Tech. Pap. Ser.* **2003**, 2003-01-3205.

(17) Szybist, J. P.; Boehman, A. L.; Taylor, J. D.; McCormick, R. L. Evaluation of Formulation Strategies to Eliminate the Biodiesel NO_x Effect. *Fuel Process. Technol.* **2005**, *86*, 1109−1126.

(18) Sharp, C. A.; Howell, S. A.; Jobe, J. The Effect of Biodiesel Fuels on Transient Emissions from Modern Diesel Engines, Part II Unregulated Emissions and Chemical Characterization. *SAE Tech. Pap. Ser.* **2000**, 2000-01-1968.

(19) McCormick, R. L.; Graboski, M. S.; Alleman, T. L.; Herring, A. M. Impact of Biodiesel Source Material and Chemical Structure on Emissions of Criteria Pollutants from a Heavy-Duty Engine. *Environ. Sci. Technol.* **2001**, *35*, 1742−1747.

(20) Krahl, J.;. Munack, A.; Schröder, O.; Stein, H.; Bünger, J. Influence of Biodiesel and Different Designed Diesel Fuels on the Exhaust Gas Emissions and Health Effects. *SAE Tech. Pap. Ser.* **2003**, 2003-01-3199.

(21) Alam, M.; Song, J.; Acharya, R.; Boehman, A.; Miller, K. Combustion and Emissions Performance of Low Sulfur, Ultralow Sulfur and Biodiesel Blends in a DI Diesel Engine. *SAE Tech. Pap. Ser.* **2004**, 2004-01-3024.

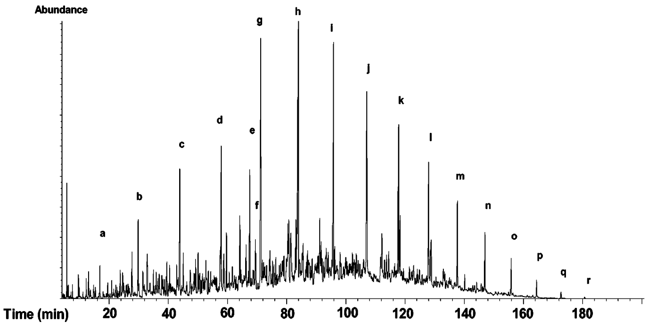

Figure 1. GC-MS trace (total ion chromatogram) of the petrodiesel base fuel used in this work. The peaks of the following fuel components are labeled by the corresponding letters in order of retention time: (a) nonane, (b) decane, (c) undecane, (d) dodecane, (e) 2-methylnaphthalene, (f) 1-methylnaphthalene, (g) tridecane, (h) tetradecane, (i) pentadecane, (j) hexadecane, (k) heptadecane, (l) octadecane, (m) nonadecane, (n) eicosane, (o) heneicosane, (p) docosane, (q) tricosane, and (r) tetracosane.

Table 2. Fatty Acid Profiles (wt %) of Commercial Biodiesel and Technical Grade Methyl Oleate Fuels Used in this Work

	fatty acid methyl ester fuel	
fatty acid[a]	methyl oleate (technical grade)	methyl soyate (commercial biodiesel)
14:0	3.26	–
16:0	5.59	11.00
18:0	–	4.13
18:1 Δ9 *c*	76.77	24.53
18:1 Δ9 *t*	2.95	–
18:1 Δ11	1.73	0.62
18:2	9.71	53.37
18:3	–	6.35

[a] Systematic (trivial) names of the fatty acid methyl esters in this table from top to bottom: methyl tetradecanoate (methyl myristate), methyl hexadecanoate (methyl palmititate), methyl octadecanoate (methyl stearate), methyl 9(*Z*)-octadecenoate (methyl oleate), methyl 9(*E*)-octadecenoate (methyl elaidate), methyl 11(*Z*)-octadecenoate (methyl vaccenate), methyl 9(*Z*),12(*Z*)-octadecadienoate (methyl linoleate), methyl 9(*Z*),12(*Z*),15(*Z*)-octadecatrienoate (methyl linolenate).

Technical grade methyl oleate, neat methyl palmitate (systematic name: methyl hexadecanoate), methyl laurate (systematic name: methyl dodecanoate), hexadecane, and dodecane were obtained from Sigma-Aldrich (Milwaukee, WI). Four hundred parts per million of proprietary diesel fuel lubricity additive (Lubrizol; Wickliffe, OH) was added to the hexadecane and dodecane fuels since they were suspected to possess poor lubricity[22] and therefore could cause engine damage. Table 2 gives the fatty acid profile of the technical grade methyl oleate and commercial biodiesel used here. Table 3 lists various properties of the fuels studied here.

GC analyses for determining the fatty acid profile of the methyl ester fuels were carried out on a Varian (Palo Alto, CA) 3400 CX gas chromatograph equipped with a flame-ionization detector and a Supelco SP-2380 capillary column (30m × 0.25 mm; 0.2 μm film thickness). The oven temperature program was 150 °C for 15 min, ramp 150–210 °C at 2 °C/min, 50 °C/min to 220 °C with a final 5 min hold time. Retention times were verified against authentic samples of individual pure fatty acid methyl esters. All relative percentages determined for each fatty acid methyl ester sample are the means of triplicate runs. GC-MS analyses for analyzing the petrodiesel base fuel were conducted on an Agilent Technologies (Palo Alto, CA) 6890 gas chromatograph equipped with a 30 m × 250 μm × 0.50 μm HP5-MS capillary column coupled to an Agilent Technologies 5973 mass-selective detector. The oven temperature program was constant at 30 °C for 10 min, ramp 30–250 °C at 1 °C/min, then 5 °C/min to 270 °C with a final 10 min hold time. GC and GC-MS analyses showed a purity for the methyl laurate and methyl palmitate fuels of >99% and for the dodecane and hexadecane fuels of >98%.

Lubricity was determined with a high-frequency reciprocating rig (HFRR) lubricity tester according to the standard ASTM D6079 (**2**). Kinematic viscosity was analyzed at 40 °C with a Cannon-Fenske capillary viscometer according to the standard ASTM D445 and was in the appropriate range.[23] Acid values were obtained using AOCS (American Oil Chemists' Society) method Cd 3d-63. The cetane numbers of the test fuels were also determined in an ignition quality tester (IQT) following the standard ASTM D6890 and were in the range of previously published data.[24] A Phase Technology (Richmond, BC, Canada) cloud, pour, and freeze point analyzer was used for cloud point determination.

Exhaust Emissions Testing. The test engine was a 2003 model year DDC (Detroit Diesel Corporation) Series 60 diesel engine with direct injection, six cylinders, 14 L displacement, turbocharging, intercooling, and electronic control. The fuel system of the engine incorporates high-pressure electronic unit injectors. The engine was equipped with a high-pressure loop EGR (exhaust gas recirculation) system incorporating an EGR cooler with engine jacket water as the cooling medium. Engine control input was achieved electronically via wiring the feedback output of the test cell servo controller directly to a connection point on the engine wiring harness. The engine employed an intake air humidity and temperature sensor which was installed into the test cell intake air system ducting upstream of the turbocharger compressor inlet.

A time delay occurred between the testing of the methyl laurate fuel and the other fuels (hydrocarbons and methyl esters) because of a delivery delay. In the meantime, a new turbocharger with the same part number had to be installed on the test engine. With the new turbocharger, the engine produced overall lower PM levels than with the old turbocharger. Therefore, exhaust emission levels with fuels tested before and after the turbocharger change cannot be directly compared. Rather, it is necessary to compare the relative change in exhaust emissions to the appropriate base fuel data obtained for the test fuel. Base fuel exhaust emissions for comparison with methyl laurate are therefore reportedly separately.

All emissions tests were conducted according to procedures given in the Code of Federal Regulations (CFR) Title 40 Part 86 (Control of Emissions from New and In-Use Highway Vehicles and Engines), Subpart N, using a heated flame ionization detector for hydrocarbons, chemiluminescence detection for NO_x, nondispersive infrared detection for CO and Pallflex (Pall Corp., East Hills, NY) T60A20 filters for PM, with the soluble organic fraction (SOF) of the PM extracted with a Soxhlet apparatus using a 70:30 ethanol/

Table 3. Properties of the Fuels Used in the Present Work

fuel	cetane no. (IQT)	cloud point (°C)[a]	kinematic viscosity (mm^2/s)	lubricity by HFRR (wear scar; 60 °C; μm)[a]	acid value
petrodiesel	46.7/46.9[a,b]	−16.1/−16.4	2.38	553; 565	nd[c]
biodiesel[d]	54.0	1.1/1.3	4.17	190; 175	0.112
hexadecane	102.6	nd	2.92	306; 330[e]	nd
dodecane	78.9	nd	1.45	232; 230[e]	nd
methyl laurate	60.4	nd	2.49	251; 308	0.446
methyl palmitate	88.0	nd	4.37	115; 98	0.000
methyl oleate[d]	58.9	−12.6/−12.8	4.52	217; 208	2.006

[a] Duplicate determination. [b] Cetane number 51.1 according to ASTM D613 (cetane engine). Cetane index 48.8 according to ASTM D976. [c] nd = not determined. [d] For the fatty acid profile of biodiesel and technical grade methyl oleate, see Table 2. [e] With lubricity additive. For lubricity without an additive, see ref 22.

Table 4. Regulated Exhaust Emissions of the Fuels Tested in the Present Work[a]

fuel	exhaust emissions species (g/hp hr)			
	HC	CO	NO_x	PM
petrodiesel (av)	0.06(0.017)	0.53(0.048)	2.27(0.095)	0.109(0.005)
hexadecane	0.02(0.008)	0.39(0.016)	1.91(0.036)	0.060(0.002)
dodecane	0.06(0.018)	0.45(0.055)	1.92(0.054)	0.055(0.001)
methyl soyate	0.04(0.024)	0.40(0.003)	2.55(0.007)	0.024(0.001)
methyl oleate	0.03(0.011)	0.27(0.011)	2.41(0.015)	0.029(0.001)
methyl palmitate	0.05(0.018)	0.30(0.020)	2.17(0.012)	0.020(0.001)
petrodiesel[b]	0.04(0.022)	0.45(0.003)	2.08(0.017)	0.077(0.003)
methyl laurate[b]	0.05(0.008)	0.32(0.011)	1.98(0.022)	0.013(0.000)

[a] Standard deviations given in parentheses. [b] New turbocharger. Value for methyl laurate relative to the second run of the petrodiesel base fuel. The second run of the petrodiesel base fuel showed a work reduction of −0.6%.

toluene solvent system. The maximum fuel quantity was adjusted for each fuel so that the same work was achieved regardless of the energy content of the fuel. Emission measurements were carried out over the heavy-duty transient FTP, and only hot-start transient emission testing was performed. Repeat hot-start tests were performed on each fuel to characterize the regulated exhaust emissions levels of the engine operating on a given fuel. Test runs with the base petrodiesel fuel were included on several test days to help assess the effect of day-to-day variability on the fuel comparisons. Triplicate test points were taken for each fuel with the exception of the base petrodiesel fuel which was tested several times. The averaged exhaust emissions data with standard deviations are given in Table 4, while the results of all individual tests are given elsewhere.[25] A hot-water bath was used for liquefying methyl palmitate (mp 30 °C) in its drum. The test cell fuel system was controlled to 38 ± 3 °C during testing; thus methyl palmitate did not present any additional handling problems once liquefied. No other operational problems with the fuels were observed.

Results and Discussion

One commercial petrodiesel fuel as base fuel, one commercial biodiesel fuel, and two neat alkane components of petrodiesel (hexadecane and dodecane) as well as two neat methyl ester fuels (methyl palmitate and methyl laurate) and one technical grade methyl ester fuel (methyl oleate) were investigated for their generation of regulated exhaust emissions species in a 2003 heavy duty diesel engine with turbocharging and exhaust gas recirculation (EGR). EGR has been shown to reduce NO_x exhaust emissions.[26] Table 4 presents the actual values observed for the various regulated exhaust emissions species when testing the fuels. Figure 2 shows the percent change in NO_x and PM exhaust emissions for the various hydrocarbon and methyl ester fuels versus petrodiesel resulting from the data in Table 4. Figure 3 is an analogous depiction of the percent change but for HC and CO exhaust emissions. Table 5 contains the results of the SOF analyses. Table 6 lists the CO_2 emissions, brake-specific fuel consumption (BSFC), and the work (hp hr) achieved with each fuel as well as the related differences (%) of the various test fuels compared to the base fuel.

The results in Table 4 and Figures 2−3 display several interesting changes in the effect of compound structure on combustion and exhaust emissions compared to previous results. Differences in the NO_x and PM species of methyl laurate versus methyl palmitate are minor. The same observation holds for dodecane and hexadecane. Therefore, contrary to previous results,[19] chain length, at least in the range studied here, has only a minor to negligible effect on NO_x exhaust emissions.

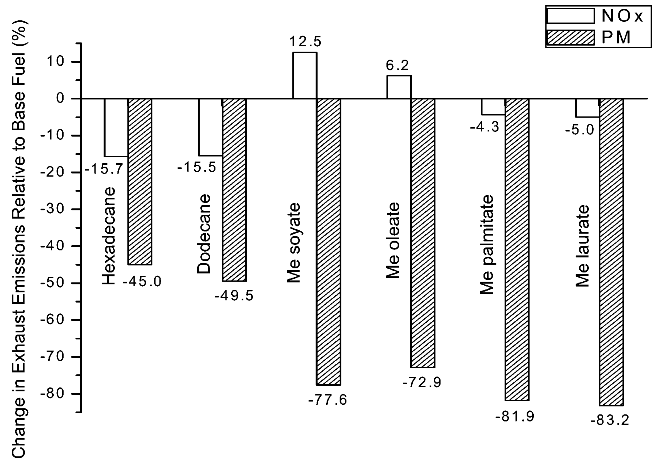

Figure 2. Change (%) in NO_x and particulate matter exhaust emissions relative to the petrodiesel base fuel in the present work. Values for methyl laurate obtained with new turbocharger (see Experimental Section). The petrodiesel base fuel showed the following values with the new turbocharger: HC, −31.8%; CO, −15.1%; NO_x, −15.1%; PM, −29.4%.

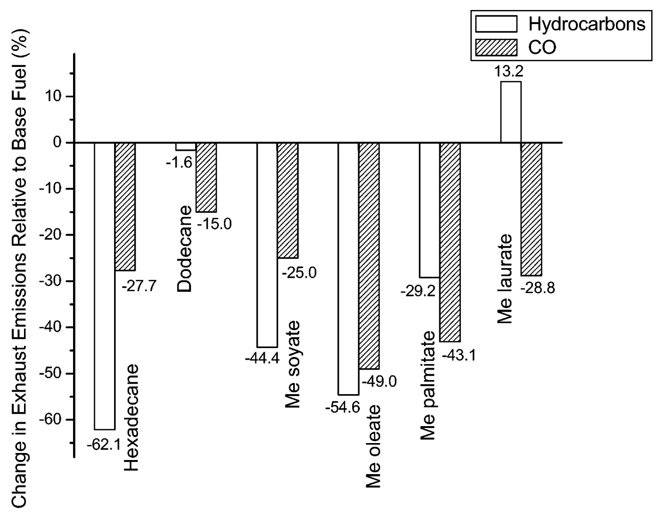

Figure 3. Change (%) in hydrocarbon and CO exhaust emissions relative to the petrodiesel base fuel in the present work. Values for methyl laurate obtained with new turbocharger (see also caption for Figure 2).

Table 5. SOF Analyses[a]

fuel	SOF (%)	SOF (mg/hp h)	PM (g/hp hr)
petrodiesel	14.9; 9.0	15.3; 10.0	0.103; 0.111
hexadecane	3.1; 8.3	1.8; 5.2	0.059; 0.063
dodecane	4.3; 3.6	2.4; 5.2	0.055; 0.055
methyl soyate	36.2; 36.7	8.7; 8.7	0.024; 0.24
methyl oleate	33.0; 30.1	9.9; 9.0	0.030; 0.030
methyl palmitate	18.1; 10.5	3.6; 2.1	0.020; 0.020
methyl laurate	37.5; 38.1	4.9; 4.8	0.013; 0.013

[a] Two determinations for each fuel.

(22) Knothe, G.; Steidley, K. R. Lubricity of Components of Biodiesel and Petrodiesel. The Origin of Biodiesel Lubricity. *Energy Fuels* **2005**, *19*, 1192−1200.

(23) Knothe, G.; Steidley, K. R. Kinematic Viscosity of Biodiesel Fuel Components. Influence of Compound Structure and Comparison to Petrodiesel Fuel Components. *Fuel* **2005**, *84*, 1059−1065.

(24) Knothe, G.; Matheaus, A. C.; Ryan, T. W., III. Cetane Numbers of Branched and Straight-Chain Fatty Esters Determined in an Ignition Quality Tester. *Fuel* **2003**, *82*, 971−975.

(25) Ryan, T. W., III; Sharp, C. A.; Knothe G. Heavy-Duty Diesel Engine Emissions Tests Using Special Biodiesel Fuels. *SAE Tech. Pap. Ser.* **2005**, 2005-01-3671.

(26) Tsolakis, A.; Megaritis, A.; Wyszynski, M. L. Application of Exhaust Gas Reforming in Compression Ignition Engines Fueled by Diesel and Biodiesel Fuel Mixtures. *Energy Fuels* **2003**, *17*, 1464−1473.

Table 6. CO_2 Exhaust Emissions, Work, and Brake-Specific Fuel Consumption (BSFC)[a]

fuel	CO_2 (g/hp h)	BSFC (g/hp h)	work (hp h)
petrodiesel (av)	595.12(8.05)	187.42(2.56)	33.07
hexadecane	560.4(0.79)	180.46(0)	32.73(−1.0)
dodecane	588.57(28.73)	190.16(9.16)	32.21(−2.6)
methyl soyate	595.7(1.22)	210.54(0.43)	32.75(−1.0)
methyl oleate	592.57(5.91)	209.30(1.88)	32.72(−1.1)
methyl palmitate	575.8(7.23)	205.57(1.14)	32.76(−0.9)
petrodiesel[b]	570.27(2.46)	179.72(0.75)	
methyl laurate[b]	568.1(18.09)	200.84(6.21)	32.88(−3.0)

[a] Values in parentheses are standard deviations for CO_2 and BSFC and difference (%) in work vs. the petrodiesel base fuel. [b] New turbocharger. Value for methyl laurate relative to the second run of the petrodiesel base fuel.

However, for increasing unsaturation, increasing NO_x exhaust emissions are still observed. Thus, the difference in cetane number, at least in the range studied here, between hexadecane and dodecane on the one side and methyl palmitate and methyl laurate on the other side does not affect NO_x exhaust emissions. The same holds for properties such as kinematic viscosity and bulk modulus which apparently have no or little effect on NO_x under the present test conditions. However, these properties can have opposing effects on exhaust emissions, so the possibility exists that their effects cancel out, leading to the appearance that there is no effect. In any case, the effects differ from previous studies, since, as mentioned above, no influence of chain length is observed. Another possibility is that the increase in NO_x exhaust emissions observed with increasing unsaturation under the present conditions may also have other causes. In the newer-technology engine used here, the fuel property most likely affecting NO_x exhaust emissions is the adiabatic flame temperature.[25] Also, in a study on cetane numbers, it was shown that chemical structure may play a role through the precombustion formation of intermediate compounds with low cetane numbers primarily from more unsaturated fatty compounds.[27] Although cetane number, as mentioned above, may not be significant under the present conditions, a similar effect may still be at work in that such intermediates, and their physical properties affect combustion and exhaust emissions.

Nevertheless, the major factors affecting the exhaust emissions of biodiesel and its components compared to petrodiesel and its alkane components are the presence of the methyl ester group and unsaturation. The oxygenated methyl ester group causes a significant reduction of particulate matter as shown by comparison with the two alkanes tested here while unsaturation causes a minor increase in NO_x.

A factor sometimes not considered in previous literature when reporting the relative increase or reduction of exhaust emissions of biodiesel fuels in comparison to petrodiesel is not only the fatty acid profile of the biodiesel but the composition of the petrodiesel fuel. The comparison of neat methyl ester and straight-chain alkane fuels used here establishes a baseline for comparison. The results for the exhaust emissions generated from hexadecane and dodecane versus petrodiesel clearly show the influence of the components of petrodiesel on emissions. For that reason, it is of interest to note the composition of the petrodiesel used here (Figure 1; some prominent components highlighted in this figure). In addition to straight-chain alkanes, petrodiesel contains various alkylated mono- or polyaromatic compounds and branched alkanes, to which virtually all the unlabeled peaks in Figure 1 can be attributed. Although to the best of our knowledge, no emissions studies of such neat compounds have been conducted, the implication is that the components of petrodiesel that are not straight-chain alkanes would cause an increase in exhaust emission compared to the base fuel since the emission-reducing effect of the straight-chain alkanes must be compensated to attain the emissions level of the base fuel. That branched hydrocarbons may generate less favorable exhaust emissions than their straight-chain counterparts may be indicated by a highly branched compound, 2,2,4,4,6,8,8-heptamethylnonane, being the low-quality reference material on the cetane scale. Relatedly, the emissions of biodiesel fuels compared differently to various petrodiesel fuels in some previous studies.[20−21]

Since the composition of the petrodiesel fuels in exhaust emissions studies varies just as the fatty acid profile of the biodiesel fuels varies, the results presented here offer an insight on how the petrodiesel fuel composition can affect the comparison of exhaust emissions: generally, the greater the straight-chain alkane composition of the petrodiesel fuel, the more favorable its exhaust emissions in comparison to biodiesel fuel. However, the most significant difference between straight-chain alkanes and fatty acid methyl esters is observed for PM exhaust emissions, the biodiesel components being by far more advantageous. Indeed, a comparison of the PM exhaust emissions observed under the present conditions show that biodiesel and its components almost meet future regulations regarding these species. Although further research is required, this may render the use of particulate traps unnecessary if a diesel oxidation catalyst is employed when using neat biodiesel as fuel.

The soluble organic fraction (SOF) of the PM was significantly higher with the biodiesel and neat methyl ester fuels (Table 5). This result corresponds with previous research[28] which showed that the SOF increases with biodiesel, although a dependence on the engine test conditions and PM sampling parameters can be observed. Although the exact mechanism requires some research in light of some varying results concerning petrodiesel versus biodiesel components, the higher SOF observed with biodiesel and the neat methyl ester fuels can probably be attributed to the lower volatility (higher boiling point) of biodiesel.[28]

Fuel consumption was lowest for petrodiesel and the two alkanes, while it was highest for methyl soyate and the technical grade methyl oleate (Table 6). The two saturated methyl esters gave slightly lower fuel consumption than the two more unsaturated methyl ester fuels.

Summary and Conclusions

The exhaust emissions of commercial biodiesel and petrodiesel, three components of biodiesel fuels, methyl laurate, methyl palmitate, and methyl oleate (technical grade), and two components of petrodiesel, dodecane and hexadecane, were studied in a 2003 model year heavy-duty 14 L six-cylinder diesel engine with EGR. The commercial biodiesel fuel, as well as the fatty compounds, significantly reduced PM exhaust emissions (75−83%) compared to the petrodiesel base fuel, while the two hydrocarbons found in petrodiesel achieved reductions of only 45−50%. However, NO_x exhaust emissions were slightly increased with commercial biodiesel and technical grade methyl oleate, while methyl laurate and methyl palmitate as well as

(27) Knothe, G.; Bagby, M. O.; Ryan, T. W., III. Precombustion of Fatty Acids and Esters of Biodiesel. A Possible Explanation for Differing Cetane Numbers. *J. Am. Oil Chem. Soc.* **1998**, *75*, 1007−1013.

(28) Chang, D. Y.; Van Gerpen, J. H. Determination of Particulate and Unburned Hydrocarbon Emissions from Diesel Engines Fueled with Biodiesel. *SAE Tech. Pap. Ser.* **1998**, *982527*.

dodecane and hexadecane led to a slight decrease of NO_x compared to the base fuel. The chain length of the compounds had little effect on NO_x and PM exhaust emissions, while the influence was greater on HC and CO, the latter being reduced with decreasing chain length. Unsaturation in the fatty compounds causes an increase in NO_x exhaust emissions. The present results differ from previous literature data showing the effect of newer engine technology on exhaust emissions. The low levels of PM observed with the ester fuels may influence emissions reduction technologies when using biodiesel.

Acknowledgment. We thank Kevin R. Steidley (USDA/ARS/NCAUR) for excellent technical assistance.

EF0502711